

132 Declaration
USSN 10/669,956

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PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of)
)
Haiyou Wang et al.) Art Unit 1754
)
Serial No. 10/669,956) Before the Examiner
)
Filed: September 23, 2003) Cam N. Nguyen
)
**CO-FREE HYDROGEN FROM DECOMPOSITION
OF METHANE**

DECLARATION UNDER 35 U.S.C. 1.132

R. Terry K. Baker declares and says:

That he is a named inventor on the instant application.

That he has read and understands the Office Action dated December 08, 2004.

That he has read and understands Choudhary et al. (USP 5,756,421).

That it is the Examiner's position that Choudhary discloses a process for preparing a composite catalyst that is useful for the oxidative conversion of methane or natural gas to H₂ and CO (synthesis gas) and that the composite catalyst consists of transitional and alkaline earth metal oxides having the formula: T_mAO_n, wherein T is a transition element selected from Ni, Co, Pd, Ru, Rh, Ir and mixtures thereof, m is the mole ratio of T/A, which mole ratio is from about 0.01 to about 10; A is an alkaline earth element selected from Mg, Ca, Ba, and Sr and mixtures thereof, and n is the number of oxygen atoms needed to complete the valence requirement of the transition and alkaline earth elements.

That it is also the Examiner's position that it would have been prima facie obvious to one of ordinary skill in the art at the time the invention was made to have optimized the nickel concentrations in the process of Choudhary in order to achieve an effective catalyst or a

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catalyst composition having the desired Ni concentrations because it is known in Richter to produce a catalyst having Ni in the amount of up to 89.5% by weight.

That he has had conducted, under his supervision, the following experiments to show that the catalysts of the present invention are not the same, nor are they obvious to one having ordinary skill in the art, in view of Choudhary et al.

PREPARATION OF CATALYSTS

Preparation of Comparative Choudhary et al.

A NiO-MgO catalyst having a Ni/Mg mole ratio of 1.0 was prepared according to the procedure presented in Example 15 of US Patent 5,175,421 to Choudhary et al.

A mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and MgCO_3 in a ratio of 3:1 was finely ground and made into a paste with the addition of de-ionized water. This paste was subsequently dried in air at 120°C overnight. This powder was heated in air at 590°C in order to convert the respective metal salts to metal oxides. Following this step the powdered oxide mixture was subjected to ball milling for 24 hours to reduce the particle size. The NiO-MgO catalyst was calcined in air at 910°C for 5 hours, and is designated "Catalyst A". In a second experiment the above calcined NiO-MgO catalyst was reduced in a 20% H_2 /He mixture at 500 °C for 2.0 hours, designated "Catalyst B". Both Catalyst A and Catalyst B are comparative catalysts and catalyst of Choudhary et al.

Preparation of Catalyst of the Present Invention – Catalyst C

A mixture of nickel nitrate and magnesium nitrate were mixed in a desired ratio and were initially dissolved in ethanol to form a homogeneous solution. This solution was then subjected to an evaporation step as the temperature was gradually raised from 22° to 150°C. The resulting solid mass of substantially uniformly mixed nickel and magnesium salts(nitrates) was then calcined in flowing air at 500°C for 5 hours in order to covert the metal nitrates to the respective metal oxides. The mixed metal oxide granules were then ground to a fine powder in a ball mill for a period of 60 hours.

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Finally, the oxide powder was reduced in flowing 20%H₂/He mixture at 850°C for 2 hours. These conditions were sufficient to convert substantially all of the nickel oxide to the metallic state whereas the magnesium component remained in the oxide form.

USE OF CATALYSTS IN METHANE REACTION

Each of the three catalysts prepared above were subsequently reacted in the presence of methane in a quartz flow reactor heated by a Lindberg horizontal tube furnace. The gas flow to the reactor was precisely monitored and regulated by the use of MKS mass flow controllers allowing a constant composition of feed to be delivered. Powdered catalyst samples (50 mg) were placed in a ceramic boat at the center of the reactor tube in the furnace and the system flushed with argon for 0.5 hours prior to reaction in 60 ml/min methane at 550°C for 5 hours. The progress of the reaction was followed as a function of time by sampling both the inlet and outlet gas streams at regular intervals and analyzing the reactants and products by gas chromatography. Any solid carbon deposited during the time on stream was determined gravimetrically after the system had been cooled to room temperature. The results are presented in Table I below.

TABLE I

Catalyst	Calcination Temp (°C)	Reduction Temp (°C)	%CH ₄ Conversion	H ₂ yield (L-H ₂ /g-Cat)	Solid Carbon Yield (g-C/g-Cat)
A (Comparative)	910	-	0	0	0
B (Comparative)	910	500	0	0	0
C(This Invention)	500	850	17.2	107	29

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Examination of the data presented in Table I above shows dramatic differences in the ability of the Comparative Catalysts (A and B) versus the Catalyst of The Present Invention (Catalyst C) to decompose methane into hydrogen and solid carbon. It is evident that Catalysts A and B that had been subjected to a calcination temperature of 910°C exhibited no activity for this reaction. Furthermore, a reduction treatment at 500°C in hydrogen (Catalyst B) prior to reaction in methane failed to stimulate catalytic activity. On the other hand, when the initial calcination step was conducted at 500°C and followed by a reduction in hydrogen at 850°C (a preparation procedure of the present invention), the resulting catalyst (Catalyst C) exhibited a significant degree of catalytic activity.

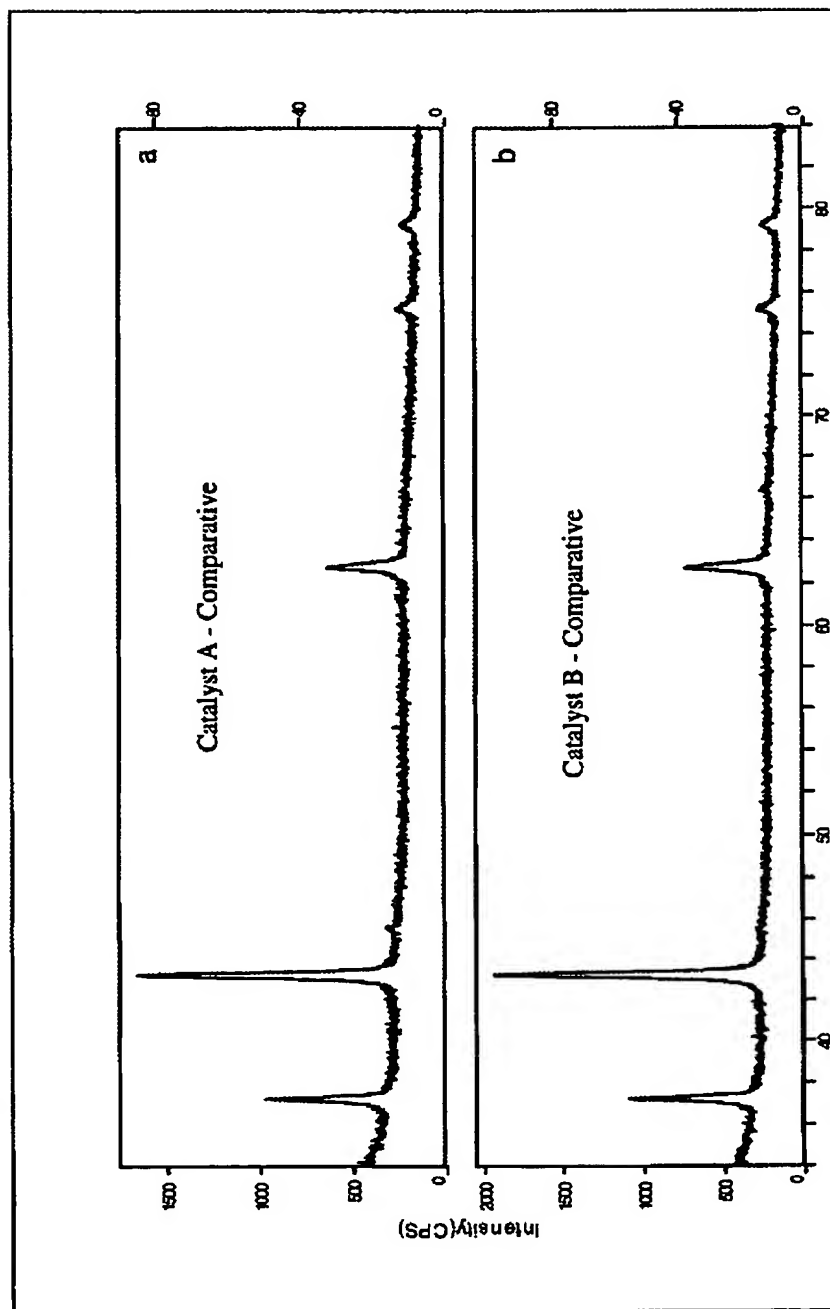
ANALYSIS OF CATALYST COMPOSITION

The three catalysts were analyzed by X-ray diffraction which was performed in a Rigaku Multiflex diffractometer with monochromatized Cu K α radiation. From the X-ray patterns shown in Figures 1 and 2 hereof it is apparent that when the catalyst is calcined in air at 910°C (Catalyst A) then even following a subsequent treatment in H₂ at 500°C (Catalyst B), the Ni component remains in the form of an oxide and solid solution. In contrast, when the catalyst is prepared in accordance to the present invention a catalyst results wherein at least 25% of the nickel component is in the catalytically active metallic state.

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Figure 1

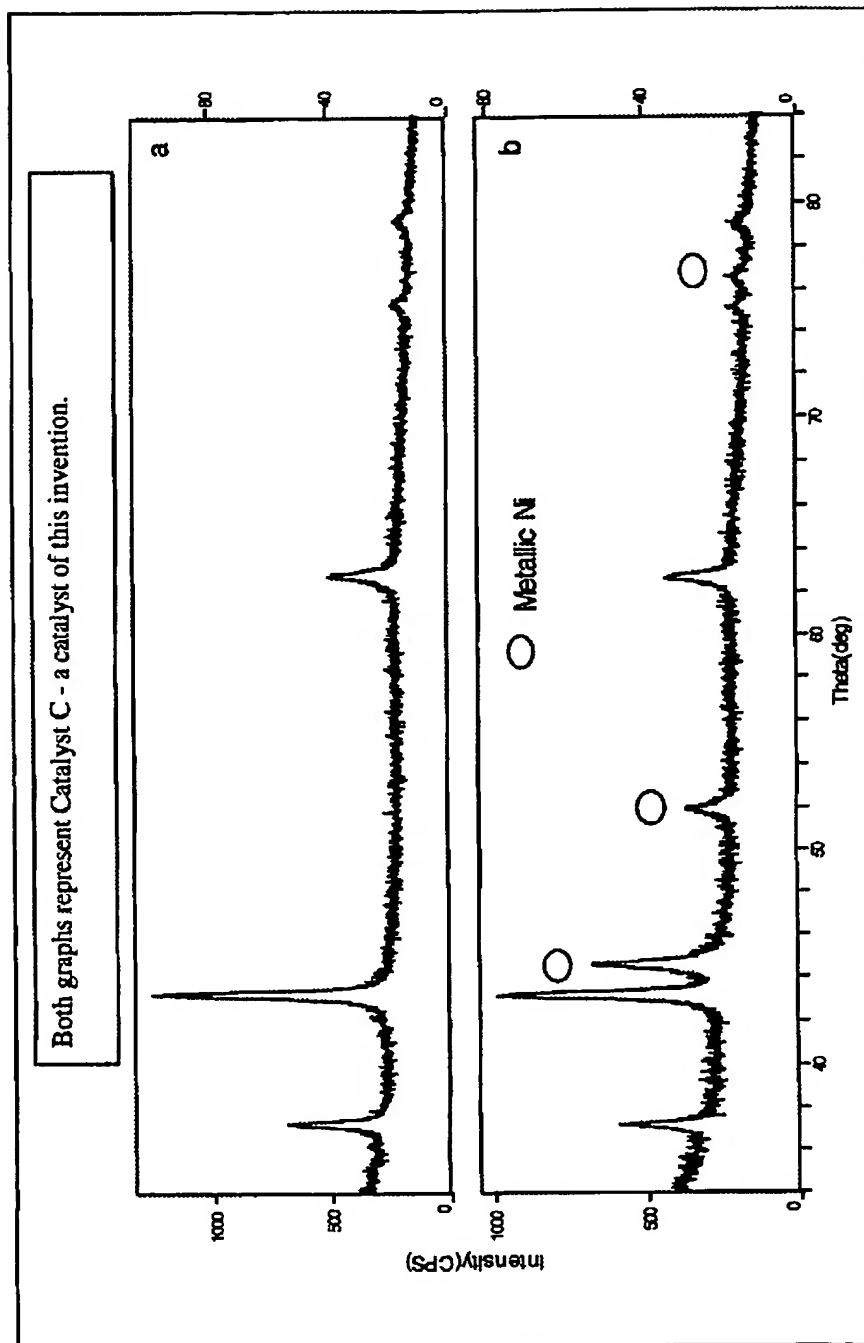
XRD patterns of NiO-MgO (Ni:Mg=1:1) after calcination at 910°C (a), designated "Catalyst A" and after further reduction at 500°C (b, designated as "Catalyst B".



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Figure 2

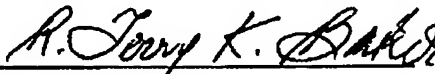
XRD patterns of NiO-MgO (Ni:Mg=1:1) after calcination at 500°C (a) and after further reduction at 850°C (b), which is designated as "Catalyst C".



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I hereby declare that all statements made herein are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date 4/01/05


R. Terry K. Baker